

Study on Ketalization Reaction of Polyvinylalcohol by Ketones. II. Behavior of Polyvinylketal, Obtained by Acetone, in Water

NAOFUMI NAKAMURA, *Tezukayama College, Gakuen-Minami, Nara 631, Japan*

Synopsis

Films prepared from polyvinylketal obtained by acetone, with different ketalization degree, were soaked in water and degree of swell, solubility, and hydrolysis of films were measured. The reaction of film with water, in acidic side, easily proceeds even at lower temperature ranges, and at first film swells, and then as deketalization reaction proceeds the film dissolves in water. Polyvinylketal of the ketalization degree below 5 mol% behaves similarly to polyvinylalcohol (PVA). With polyvinylketal of the ketalization degree of above 5 mol%, dissolution time is controlled by both ketalization degree and pH of water which reveals that deketalization reaction proceeds proportional to proton concentration. On the other hand, in neutral or alkaline conditions where hydrolysis does not proceed at all, polyvinylketal of ketalization degree of 15–60 mol% dissolves in water at 0°C and therefore it can be considered as a kind of water-soluble high polymer. Polyvinylketal dissolves more easily in water at lower temperatures than at higher temperatures.

INTRODUCTION

As biosystems always contain water as media and water is the least expensive solvent, recent studies on the behavior of high polymeric matters in water are prevalent.¹⁻⁴ Cases where it is desired that molded goods used in living bodies disappear after a certain time lapse or in cases where a medicine-loaded swallowed capsule gradually leaches off, under certain conditions where the capsule gradually dissolves, might be possible practical ways of utilization of such biosystems.

Presently, PVA is known to be a hydrophilic polymer, but PVA dried in heat dissolves in water only at temperatures close to boiling and does not dissolve in water at room temperature. The solubility in water of polyvinylalcohol derivatives such as polyvinylformal is reported by Fujimoto et al.,⁵ who suggest that it dissolves more easily in water at lower temperature than at higher temperature. Also Sakurada and Yoshizaki⁶ prepared polyvinylformal films of various formalization degrees in several procedures and studied the behavior of films against water.

As mentioned in the previous report,⁷ the author successfully obtained polyvinylketal from acetone and PVA, but as the values of equilibrium constant are extremely low, it is expected that polyvinylketal is easily hydrolyzed by water. Elucidating the behavior of polyvinylketal against water serves not only in establishing purificating conditions of the polymer but also

extends possible means of utilization as a water-soluble polymer. Therefore, studies of degree of swell, solubility, deketalization degree, and so on with polyvinylketal films of various ketalization degree soaked in water of several pH values at various temperatures were made and reported.

EXPERIMENTAL PROCEDURE

Samples

All polyvinylketal (PVKL) samples obtained by acetone were synthesized by the method described in the previous report.⁷

Film Preparation Method

PVKL dissolved in ethanol at concentration of 5 wt% is gradually allowed to dry on a glass plate at 20 to 30°C for 4 to 5 days, and in this way transparent film is obtained. In order to observe effects of crystallization by heat, film thus obtained is dried at room temperature under vacuum until the solvent is thoroughly removed from the film. Ethanol 100% was used as solvent for PVKL of ketalization degree of above 35 mol%; for ketalization degree of 10–35 mol%, 80% ethanol aqueous solution; for ketalization degree of 5–10 mol%, 50% ethanol aqueous solution; for ketalization degree of less than 5 mol%, 25% ethanol aqueous solution was used. For comparison, PVA used was prepared into film with water as solvent. During film preparation, hydrolysis of PVKL is not observed.

Reaction Procedure

Film, ca. 0.05 mm thick, cut into 1.5 × 3.0 cm pieces, was taken as sample. Samples were soaked in water of various pH values adjusted by HCl or NaOH kept at various prescribed temperatures, later, film is removed from water and degree of swell, solubility, deketalization, and the time needed for complete dissolution of film were measured. The dissolution of film was judged by careful observation by naked eye. As the undissolved film retains its planar form, it is not difficult to detect the time of its disappearance.

pH Value Measurement

pH Values were measured with pH meter of Hitach-Horiba, type M-7 II.

Deketalization Degree

After the reaction, acetone existing in water is quantitatively determined in iodoform method⁸ and deketalization degree was determined. Deketalization ratio is given as:

$$\text{Deketalization ratio (\%)} = \frac{\text{deketalization degree}}{\text{initial ketalization degree}} \times 100$$

Degree of Swell

Remove sample film from the water after soaking for prescribed time, lightly press both surfaces of film with filter paper to remove water, and weigh the film, W_2 g. Dry film at 105°C for 2 h and then weigh it, W_3 g. Degree of swell is given as:

$$\text{Degree of swell} = W_2/W_3$$

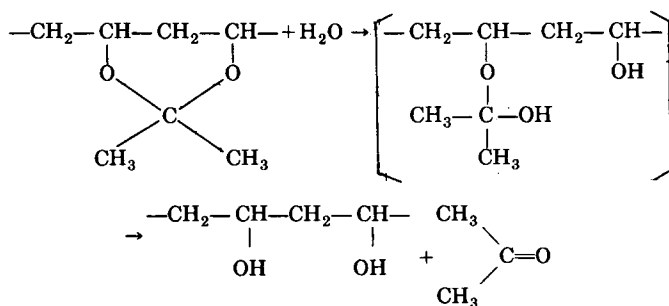
Solubility

To avoid any effect of crystallization by heat, pure polymer content of film C is determined as follows. Film samples are dried at room temperature and weighed, a (g), then dried at 105°C for 2 h and weighed it, b (g), then pure polymer content of film C is b/a . In experimental works, nonheated film is used. Film samples are dried at room temperature and weighed, W_0 (g), then the weight of pure polymer W_1 gr is $W_0 \times C$ (g). Solubility was calculated as follows:

$$\text{Solubility (\%)} = \frac{W_1 - W_3}{W_1} \times 100$$

RESULTS AND DISCUSSION

As PVKL is insoluble in water, it is considered that as hydrolysis proceeds, as shown below, it gradually becomes water soluble.⁷



Behavior of PVKL of Different Degrees of Ketalization in Acidic Water

At first, films of highly ketalized, ketalization degree (49.4 mol%) PVKL are soaked in water of various pH values at 37°C and deketalization degree, degree of swell and solubility are determined. The results are listed in Figures 1-3.

As is clear from Figure 1, PVKL is hydrolyzed with water and the rate of hydrolysis very much depends on pH value of water. At pH 2.00, in less than 10 min and at pH 3.00 at around 60 min, it is deketalized perfectly. However, in water whose pH value is considered to be almost neutral, deketalization rate is very slow, at 5 h soaking, deketalization reaction does not proceed at all and even after soaking for 24 h deketalization ratio proceeds only 5%. The

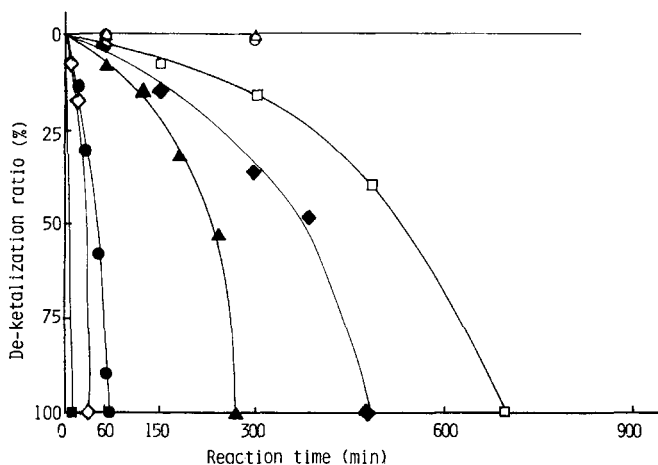


Fig. 1. Hydrolysis of PVKL in water of various pH values at 37°C. PVKL (49.4 mol%): ■ pH 2.00, ● pH 3.00, ▲ pH 3.50; □ pH 4.00, ○ pH 5.00 and 5.70; △ pH 12.00; PVKL (42.0 mol%): ◇ pH 3.00; PVKL (65.6 mol%): ◆ pH 3.00.

pH value of distilled water prepared in our laboratory is 5.70 and as discussed above the hydrolysis rate of PVKL in water whose pH value is kept close to neutral is very low, and only after standing for almost one month, PVKL does finally dissolve completely. The de-ketalization ratio in this case is ca. 80% and it must be noted that hydrolysis does not proceed to 100%. This is not due to analytical error, and the reason for this will be mentioned later. When soaked in water kept on alkaline side, PVKL swells only slightly but is very stable and does not dissolve even after being soaked for 6 months at 37°C.

In comparison with the case of de-ketalization ratio, solubility or degree of swell of PVKL in Figures 2 and 3, seems to be rather rapid at the initial stage of reaction and rather slow at the latter stage of reaction.

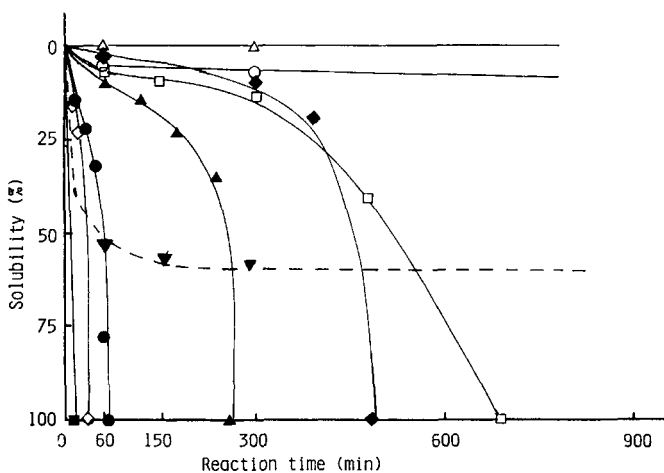


Fig. 2. Solubility of PVKL in water of various pH values at 37°C. PVKL (49.4 mol%): ■ pH 2.00, ● pH 3.00, ◆ pH 3.50; □ pH 4.00, ○ pH 5.00, and 5.70; △ pH 12.00; PVKL (42.0 mol%): ◇ pH 3.00; PVKL (65.6 mol%): ◆ pH 3.00; PVA: ▼ pH 3.00 and 5.70.

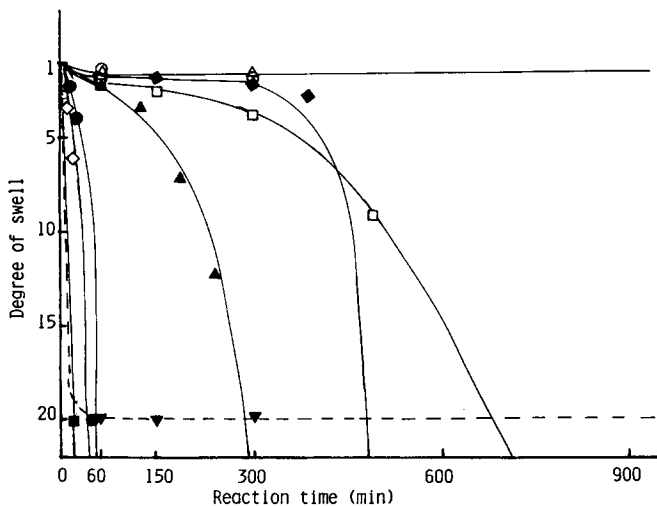


Fig. 3. Degree of swell of PVKL in water of various pH values at 37°C. PVKL (49.4 mol%): ■ pH 2.00, ● pH 3.00, ▲ pH 3.50, □ pH 4.00, ○ pH 5.00, and 5.70, △ pH 12.00; PVKL (42.0 mol%): ◇ pH 3.00; PVKL (65.6 mol%): ◆ pH 3.00; PVA: ▼ pH 3.00 and 5.70.

This is because of nonhomogeneous system reaction on film, at the early stage of reaction, water permeates into film, which causes film to swell and partially dissolve, then deketalization reaction seems to occur. In the latter stage of reaction, it is considered that as deketalization reaction proceeds and —OH group increases, either swelling or dissolution occurs.

To further elucidate this fact, PVAL of various ketalization degree and PVA, for comparison purpose, were soaked in water of various acidity at 37°C. As one representative case, hydrolysis, solubility and degree of swell at pH 3.00 are plotted in Figures 1–3. Its rate of hydrolysis depends strongly on ketalization degree and it is clear from Figure 1 that in comparison with PVKL of ketalization degree below 50 mol%, deketalization rate of No. 28 (65.6 mol%) is extremely slow.

With PVA, swelling and dissolution proceed rapidly but, even when held at 37°C for 7200 min (120 h), both degree of swell and solubility remain almost constant at values of 20 and 60%, respectively, and complete dissolution of PVA in water is not realized. This may be because PVA film is partially crystallized even it is prepared without applying heat. On the contrary, it can be considered that as ketalization reaction is carried out in homogeneous system, the PVKL thus obtained is amorphous and when hydrolyzed gives PVA of random molecular disposition, which dissolves in water of low temperature.

Effect of Acidity on Hydrolysis of PVKL

As already stated, hydrolysis reaction of PVKL largely depends on pH value of water and varies also appreciably with different degrees of ketalization. Reaction between the time needed for the complete dissolution of PVKL film and pH value of water is listed in Table I.

TABLE I
Relation Between Complete Dissolution Time and pH
with Various PVKL at 37°C

Sample	pH	2.00	2.00	3.50	4.00	5.00	5.70	12.00
No. 2	t	○	○	○	○	○	○	○
3.5%	x							
No. 22	t	5.6	9.3	11.8	9.5	11.2	15.1	4.3
8.9%	x	9.7	9.5	8.0	7.7	0	0	0
No. 44	t	6.9	8.2	24.3	43.0	39.0	28.7	65.7
15.6%	x	17.4	16.3	16.5	3.4	0	0	0
No. 31	t	5.1	19.5	19.8	9.7	19.1	16.3	21.2
19.5%	x	20.9	21.5	17.7	2.3	0	0	0.9
No. 45	t	5.8	22.8	73.8	187.8	6010	14760	
29.4%	x	31.0	30.4	29.8	28.6	14.2	12.7	△
No. 33	t	8.8	35.9	116	513	9980	25650	
42.0%	x	42.6	42.1	41.9	40.6	27.7	27.9	△
No. 25	t	9.9	69.3	265	685	34560	49773	
49.4%	x	51.2	50.3	50.6	48.5	40.2	39.3	△
No. 28	t	27.6	480	1213	2732	208650		
65.6%	x	65.6	64.6	59.3	64.6	51.7		△

t = dissolution time (min).

x = deketalization degree (mol%).

○ = no complete dissolution.

△ = insoluble.

In deketalization reaction, it is thought that using the reciprocal of dissolution time in place of hydrolysis rate constant, the mechanism of hydrolysis reaction can be estimated. In Figure 4, in accordance with results in Table I, logarithm of dissolution time is plotted against pH values.

Even though some deviation at the region above pH 5.00 and close to neutral is observed, with four kinds of PVKL at ketalization degrees exceeding

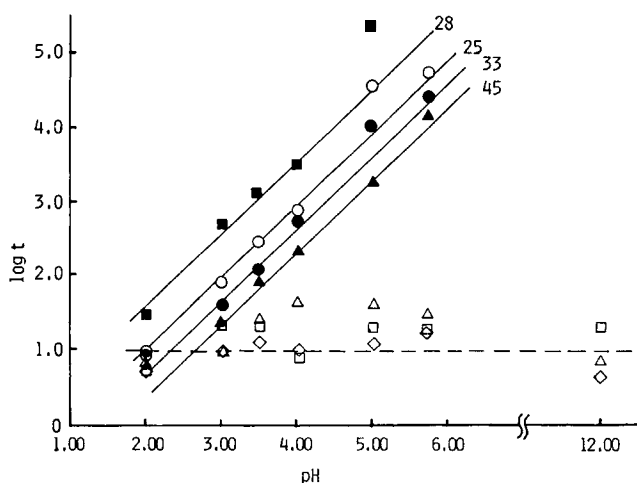


Fig. 4. Dependency of hydrolysis rate on pH values at 37°C. ◇ No. 22 (8.9 mol%), △ No. 44 (15.6 mol%), □ No. 31 (19.5 mol%), ▲ No. 45 (29.4 mol%), ● No. 33 (42.0 mol%), ○ No. 25 (49.4 mol%), ■ No. 28 (65.6 mol%).

20 mol%, No. 45 (29.4 mol%), No. 33 (42.0 mol%), No. 25 (49.4 mol%), No. 28 (65.6 mol%), respectively, linear lines of the gradient = 1 are obtained and can be expressed as formula (1) below.

$$\log t = \text{pH} + \text{const} \quad (1)$$

This shows that $1/t$ is proportional to $[\text{H}^+]$ and the deketalization reaction rate proceeds in first order to hydrogen ion concentration, $[\text{H}^+]$. With the case of acetalization reaction of PVA with aldehyde, it was already reported that the reaction rate is first order to $[\text{H}^+]^9$ and this implies that the case with ketone also proceeds in a similar mechanism.

However, with samples of ketalization degree less than 20 mol%, No. 22 (8.9 mol%), No. 44 (15.6 mol%), No. 31 (19.5 mol%), the data cannot be expressed in formula (1), and independent of pH values, in 5–40 min they completely dissolve in water. The entire difference between them and PVKL of ketalization degree above 20 mol% lies in that they are soluble even in alkaline water of pH 12.00. In these three samples, No. 22, No. 44, and No. 31, in water of pH 4.00, deketalization does not proceed at all and in water of pH higher than 5.00, dissolve without any deketalization. It is thought that in water of pH close to neutral or higher, these samples dissolve in water as PVKL. To confirm this point, samples No. 22, No. 44, and No. 31 were dissolved in water of pH higher than 5.00, excess amount of N/10 HCl was added in solutions, samples were allowed to stand for 1 h for complete deketalization, then quantitatively determined, results of which are listed in Table II.

As was expected, deketalization degrees after acidic decomposition coincide with the initial ketalization degrees within the experimental errors and by this experiment it was made clear that PVKL of ketalization degree less than 20 mol% dissolves in water of pH higher than 5.00 at 37°C without hydrolysis.

As can be seen from Table I, samples of ketalization degree above 20 mol% (No. 45, No. 33, No. 5, and No. 28) dissolve in water of pH value above 5.00 and close to neutral, even though complete deketalization is not attained for

TABLE II
Acid Decomposition of Aqueous Solution of PVKL of Ketalization Degree
of Less than 20 mol%

Sample	pH	Initial ketalization degree	Deketalization degree after being dissolved	Deketalization degree after being decomposed by HCl
No. 22	5.00	8.9	0	8.5
	5.70	8.9	0	8.5
	12.00	8.9	0	8.3
No. 44	5.00	15.6	0	15.1
	5.70	15.6	0	13.5
	12.00	15.6	0	14.9
No. 31	5.00	19.5	0	18.6
	5.70	19.5	0	19.3
	12.00	19.5	0.9	19.6

TABLE III
Behavior of PVKL, (3.5 mol%) in Water of Various pH Values at 37°C

pH	2.00	3.00	4.00	5.70
Deketalization degree (mol%)	3.1	2.6	1.7	0.5
Deketalization ratio (%)	88.6	74.3	48.6	14.3
Solubility (%)	46.0	52.8	43.1	51.2
Degree of swell	8.75	13.9	11.0	12.5

all of them. It is understood that when PVKL is deketalized to the residual ketalization degree of less than 20 mol%, it becomes soluble in water. To confirm this point, acid decomposition was carried with various samples. Deketalization degree of samples after being subjected to acid decomposition almost coincided with initial ketalization degree. Also, ketalization degrees of polymers dissolved in water were in the region of 10–15 mol% and results supporting the above-mentioned forecast were obtained.

Finally, discussion on PVKL (No. 2) of ketalization degree of 3.5 mol% is given. As listed in Table I, complete dissolution of the sample (No. 2) in water of pH value of 2.00–12.00 was not observed and it behaves similarly to PVA. Results of soaking the sample (No. 2) for 100 h in water of various pH values at 37°C are listed in Table III.

As is clear from Table III, when the sample film (No. 2) is soaked in water of pH value 2.00–5.70, even though deketalization proceeds at about 100% at lower pH value, complete dissolution in water is not observed in any case. The degree of swell is lower than that of PVA, its solubility is almost at 50%, which is close to that of PVA listed in Figure 2. It can be understood that, for cases of ketalization degree less than 5 mol%, because the crystalline part to PVA remains, molecular orientation is not randomly disposed even when subjected to deketalization, therefore, it stays insoluble in water at the relatively low temperature of 37°C.

Effect of Temperature for the Case When Dissolution and Parallel Hydrolysis Proceed

It became clear that the dissolution of PVKL in water is a two-way process: one is the dissolution by hydrolyzation of PVKL and another is the dissolution of PVKL itself. First, in order to study the effect of temperature for the case of dissolution accompanied by hydrolysis, dissolution of PVKL in water of pH value of 3.50 was studied. As it is a nonhomogeneous reaction, it is somewhat unreasonable to take the reciprocal of dissolution time as the deketalization reaction rate, but in Figure 5 logarithms of reciprocal of dissolution times are plotted against temperature. The apparent activation energies of deketalization reactions obtained from the plot for each sample are as follows: No. 22, 5.1 kcal/mol; No. 44, 7.8 kcal/mol; No. 45, 10.9 kcal/mol; No. 25, 14.0 kcal/mol; No. 28, 14.1 kcal/mol. It can be observed that in such nonhomogeneous reactions, the lower the initial ketalization degree, the easier the deketalization proceeds. In temperature ranges below 37°C, due to dissolution of PVKL itself in water which is discussed in the following paragraph, this linear relationship is not obtained.

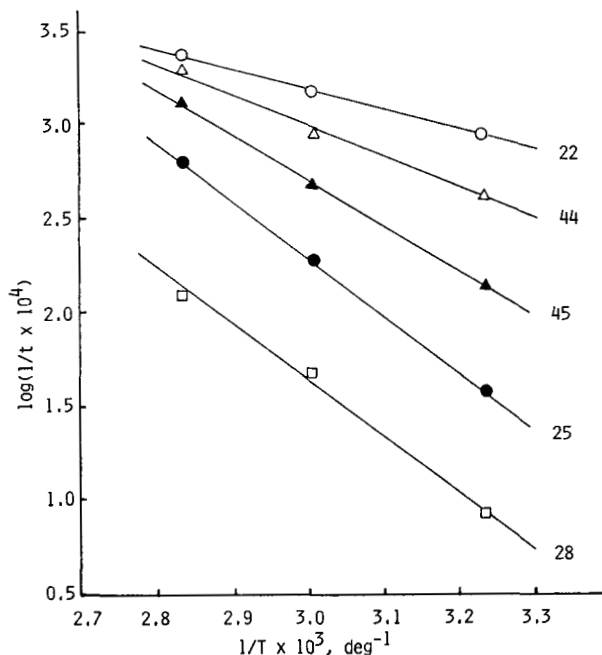


Fig. 5. Temperature dependency of deketalization reaction. \circ No. 22 (8.9 mol%), \triangle No. 44 (15.6 mol%), \blacktriangle No. 45 (29.4 mol%), \bullet No. 25 (49.4 mol%), \square No. 28 (65.6 mol%).

Effect of Temperature for the Case of Dissolution Without Accompanying Hydrolysis

As listed in Table I, it was made clear that in water close to neutral, PVKL of ketalization degree of 5–20 mol% dissolves without hydrolysis. On the other hand, when the ratio of hydrophilic portion (OH part) and hydrophobic portion (OCOCH₃) is properly adjusted in saponified polyvinylacetate obtained by partially saponifying polyvinylacetate, as the temperature increases the solubility of the polymer to water decreases and at the temperature above the cloud point, the solution, first, becomes turbid and if allowed to stand, separation into two phases is reported.¹⁰ It is also reported^{5,6} that polyvinylacetal obtained from aldehyde becomes water soluble at relatively low temperature.

The solubility in water and the cloud point of various PVKL were determined under the conditions where no hydrolysis proceeds and are plotted in Figure 6.

Distilled water of pH 5.70 was used, but similar results were obtained even with alkaline water of pH 12.00. The area within points A, B, C, and D is the region where PVKL dissolves in water without being hydrolyzed. For example, PVKL of ketalization degree 8.9 mol% expressed as point D is completely insoluble in water clearly at 0°C and even at 20°C. On the other hand, PVKL of ketalization degree of 65.6 mol% is completely insoluble in water at 0°C, but dissolves in water when heated to 60°C where deketalization degree is measured to be 56.4 mol%. With PVKL of ketalization degree of 30–50 mol%, which dissolves in water at 0°C, as the temperature increases cloud points are

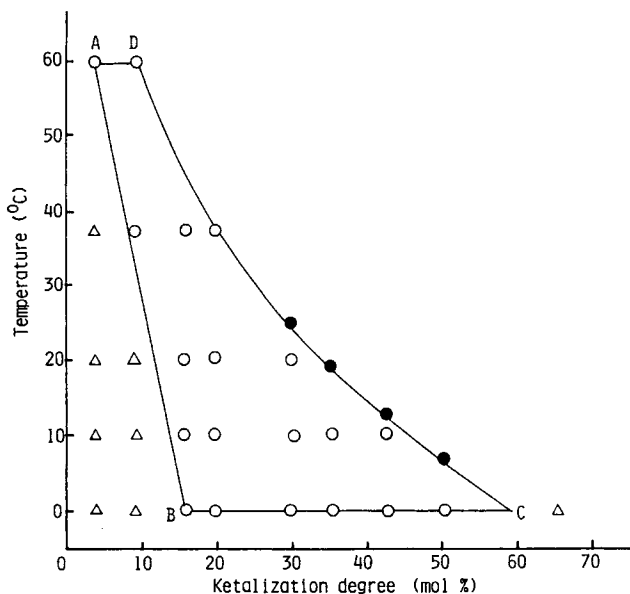


Fig. 6. PVKL vs. dissolution temperature. (Case of dissolution proceeding without any hydrolysis.) ○ dissolution, ● cloud point, △ incomplete dissolution.

observed with solutions but not with PVKL of ketalization degree of below 20 mol%. In the temperature region above 60°C, as the hydrolysis reaction starts, clear dissolution temperatures cannot be determined.

There are several speculative explanations for this, but an established theory has not been accepted. The interesting facts that polyvinylketal dissolves in slightly acidic water, even at relatively low temperature of 37°C, and in water close to neutral without any deketalization at 0°C were made clear.

The author is highly obliged to Dr. I. Sakurada, Professor Emeritus of Kyoto University, Dr. H. Matsuzaki, Professor Shinshu University, and Dr. T. Kobayashi, Toyobo Co. Ltd. for their thoughtful suggestions to the author in executing the present study. The author would like to express his sincere appreciation to Miss K. Matsumura, H. Yamamoto, and K. Nakagawa for their valuable assistance in executing experimental works.

References

1. F. Sacher and J. R. Susko, *J. Appl. Polym. Sci.*, **27**, 3893 (1982).
2. A. M. Henderson and A. Rudin, *J. Appl. Polym. Sci.*, **27**, 4115 (1982).
3. Y. Ishimaru and T. Lindstroem, *J. Appl. Polym. Sci.*, **29**, 1975 (1984).
4. H. Oyama and T. Nakajima, *J. Appl. Polym. Sci.*, **29**, 2143 (1984).
5. F. Fujimoto, T. Ohsugi, and I. Sakurada, *Chem. High Polym. Japan*, **7**, 14 (1950).
6. I. Sakurada and O. Yoshizaki, *Chem. High Polym. Japan*, **10**, 310 (1953).
7. N. Nakamura, *J. Appl. Polym. Sci.*, submitted.
8. S. Takagi, *Quantitative Analysis II*, Kyoritsu shuppan, 1980, p. 463.
9. N. Nakamura, doctoral thesis, Kyoto University (1960).
10. K. Shinoda, *Solution and Solubility*, Maruzen, 1977, p. 175.

Received March 10, 1986

Accepted June 20, 1986